



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: **0 456 373 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91303648.9**

(51) Int. Cl.⁵: **C07C 6/04, B01J 31/12**

(22) Date of filing: **23.04.91**

(30) Priority: **03.05.90 FI 902228**

(43) Date of publication of application:
13.11.91 Bulletin 91/46

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: **NESTE OY**
Keilaniemi
SF-02150 Espoo (FI)

(72) Inventor: **Hietala, Jukka**
Luhtitie 2 B 5
SF-06400 Porvoo (FI)
Inventor: **Knuuttila, Pekka**
Torpparintie 4
SF-06400 Porvoo (FI)

(74) Representative: **Lamb, John Baxter et al**
MARKS & CLERK 57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) **A catalyst for a metathesis reaction of olefines and a method for preparing the same.**

(57) **A catalyst system for metathesis reactions of olefines, especially of propylene, which system comprises a metal carbene complex on a solid carrier, in which the metal carbene complex has the formula:**



wherein M is W or Mo; R is t-butyl; y is 0 or 1; and
when y is 0, m = 3 or 4, X is Br and n is from 5 to m; and
when y is 1, m is from 1 to 4, X = Cl and n is from 4 to m.

EP 0 456 373 A1

Jouve, 18, rue Saint-Denis, 75001 PARIS

The invention relates to a catalyst for a metathesis reaction of olefines and a method for preparing the same. In the olefine chemistry, the metathesis describes the mutual exchange of carbon atoms between a double-bond pair. These reactions include e.g. the metathesis of olefines (OM), which can generally be described e.g. by means of the following reaction equation:



The metathesis reactions of olefines are not spontaneous, but they require a catalyst system containing a transitionmetal compound, which is preferably in contact with another compound (a cocatalyst) and sometimes with a third one (a promoter). The reactions are normally balance reactions, which can reach a balanced state in a couple of seconds with a good catalyst. Wolfram (W), molybdenum (Mo) and rhenium (Re) based catalysts are especially efficient, and essential are also several Ti, Nb, Ta, Re, Ru, Os and Ir systems. It is believed that the reaction is coordinatively activated by an unsaturated metal-carbene complex. The result of the reaction is also affected by the choice of a solvent, when there is a need to avoid side reactions, such as isomerization, alcylation, cyclization and addition over the double bond. For example halogenized solvents, such as chlorobenzene, are preferable solvents. It is known that the catalyst complex is carbene in solution systems and most likely also in reactions occurring with a solid carrier. Almost unexceptionally, this complex is not formed before the reaction conditions, wherein a small part of the metal changes into an active form.

Also, some metal carbenes operating without activation have been patented as a metathesis catalyst acting in a homogenous liquid phase. In general, in a heterogenous system is used a metal oxide e.g. with a silica or alumina carrier as well possibly a cocatalyst and a promoter. Typical systems include e.g. WO_3/SiO_2 , $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{Re}_2/\text{Al}_2\text{O}_3$.

In the US patent no. 4 686 314, a catalyst on an alkoxide modified carrier is described as being used in a metathesis reaction of olefines, which catalyst includes rhenium, molybdenum, wolfram and possibly a promoter, e.g. $\text{Al}(\text{OCH}(\text{CH}_2\text{CH}_3)(\text{CH}_3))_3$.

In the US patent no. 3 855 340, a catalyst has been described for a dismutation reaction of olefines according to the formula $\text{X}/\text{O}_m/\text{O}-\text{R}_{1-2n}$, wherein X is wolfram or molybdenum, and R is an alkyl group or a hydrocarbon residue. The catalyst acts in the presence of a halogenized organoaluminum compound (reduction).

In the DE publication print no. 2 213 948 is described for a conversion of olefines a catalyst according to the formula R_mMX_p in an inert matrix material, wherein M is molybdenum, wolfram or rhenium, R is hydrocarbon and X is a univalent ligand, e.g. a halogen.

The inventors have invented new catalyst complexes, which have not previously been used for catalyzing metathesis reactions.

The catalyst system in accordance with the invention is mainly characterized in that said metal carbene complex has the formula:



wherein M is W or Mo, R is t-butyl, y is 0 or 1, and

when y is 0, m = 3-4, X is Br and n is 5-m, and

when y is 1, m is 1-4, X = Cl and n is 4-m.

It has been observed that the pure or modified silica of the complexes according to the invention has active metathesis catalysts.

Advantages of the catalysts according to the invention with respect to known metathesis catalysts include:

- Owing to organic ligands, the complexes dissolve well in non-polar solvents in contrast to wolfram salts used conventionally. This results in an easy impregnation, and the distribution of the metal on the carrier is uniform.

- Part of the complexes are sublimating complexes, and they can thus be brought to the carrier also by evaporization.

- The catalyst is activated by nitrogen without an auxiliary catalyst (no air-sensitive and often pyrophoric organometal compounds, which are difficult to handle, are needed). The catalyst is activated in the reaction conditions (propylene, 400°C) without any pretreatment (the process is simplified, and no separate activation gases or regeneration gases are needed).

The preferred embodiments of the invention have the characteristics of the subclaims.

The invention is next illustrated in detail by describing the synthesis of the catalyst and the performance of the metathesis reaction itself.

The synthesization of a metal complex according to invention and its impregnation from an organic solvent

Synthesis

Metal complexes were synthesized from wolfram(IV)oxychloride WOCl_4 by substituting chloroatoms, by neopentoxide groups and oxygen by bromine or chlorine. The neopentoxide groups were derived from neopentyl alcohol $((\text{CH}_3)_3\text{CH}_2\text{OH})$ and bromine from aluminium bromide (AlBr_3) .

The structures of the complexes and the details of the synthesis have been described in the examples below. The syntheses were performed in a nitrogen atmosphere by using dried newly-distilled solvents.

The syntheses were performed in Schlenk vessels, which were in contact via a two-way cock with a separate vacuum line and a nitrogen line. An about 1 mbar vacuum was achieved in the vacuum line by means of an oil pump (Edwards 8). The line contains before the oil pump a cold trap, which is cooled by liquid nitrogen and in which the solvent fumes freeze. Pure bottle nitrogen was led to the nitrogen line, which nitrogen was as a precaution also dried with concentrated sulphur acid and neutralized with potassium hydroxide.

In all work phases were used vessels provided with cocks, which had been evacuated by opening a way to the vacuum line and then again filled with nitrogen by opening a way to the nitrogen line. When the vessels were open, a nitrogen atmosphere was maintained by means of a flow-through.

A separated synthesis product was dissolved in a small amount on pentane and transferred to a flask, in which a carrier had been weighed. The amount of the solvent used only slightly exceeded the amount the carrier was able absorb. The solvent was evaporated and it was again added several times for ensuring a uniform distribution of the dissolved complex. Finally, the catalyst was dried in a vacuum. It was loaded into a reactor tube in a nitrogen bag.

As solvents were used diethyl ether, pentane and dichloromethane, which were kept under nitrogen in a flask containing a drier. The necessary quantity of the solvent was distilled from the flask directly into the reaction vessel. Ether was dried with a potassium benzophenone mixture and dichloromethane and pentane with phosphor pentoxide.

NMR-spectra (^{13}C , ^1H) and mass spectra were run from the metal complexes and metal assays of the catalysts were performed with an atom absorption spectrometer.

Example 1

1.03 g (3.0 mmol) of wolfram(IV)oxychloride were weighed in a nitrogen bag and dissolved in 100 ml of diethyl ether. When nearly all was dissolved, 1.20 g (15 mmol) of neopentyl alcohol dissolved in 10 ml of diethyl ether were added in small quantities. It was immediately observed that the orange color of the solution had disappeared. The solution was allowed to react during a moderate mixing for one hour.

The residue was evaporated and extracted several times with a pentane-diethyl ether mixture (ca. 1:1). 1.51 g of bluish oil was obtained as an evaporation residue of the extraction solution. The product was a mixture of compounds $\text{W}(\text{O})(\text{t-BuCH}_2\text{O})_m\text{Cl}_n$, wherein $m = 1 - 4$, $n = 4 - m$ (MS).

Example 2

1.50 g (4.4 mmol) of wolfram(IV)oxychloride were weighed in a nitrogen bag and dissolved in 120 ml of diethyl ether. When nearly all was dissolved, 1.60 g (18 mmol) of neopentyl alcohol was added in small quantities. The solution was mixed for about one hour.

The evaporation residue was dissolved, whereby a complex according to Example 1 was obtained. It was dissolved in 100 ml of dichloromethane and injected in 4.4 ml (4.4 mmol) of a dibromium methane solution of AlBr_3 by simultaneously mixing the solution. The mixing continued for ca. 20 hours (a long reaction time is not necessary).

The solution was evaporated and extracted several times with pentane. 2.45 g of an orange solid substance was obtained as an extraction residue. The product is in a solid state most likely a dimer complex $\text{W}(\text{O})(\text{t-BuCH}_2\text{O})_3\text{Br}_2$ (MS, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$). The yield was ca. 90%.

The product could be sublimated (60-70°C, 1 mmHg) without a change in its structure.

Reference catalysts were also prepared for showing the functionability of the catalyst in comparison with known products.

Reference catalysts $\text{WO}_3(\text{SiO}_2)$:

Examples 3 and 4

4.5 g of ammonium wolframate $(\text{NH}_4)_2\text{WO}_4$ was weighed and distilled water was added by simultaneously mixing and sometimes warming up. The salt was dissolved, when ca. 200 ml of water had been added (a saturated solution in room temperature).

Said solution was mixed with 45.58 g of silica (PQ CS-1231, 0.6-1.6 mm) at 60-80°C for one hour. Most of the water was evaporated during three hours in a vacuum by sometimes warming up (70°C), the remainder in a heating chamber in an evaporation bowl (105°C). The catalyst was non-homogenous (it contained loose residue and the wolfram content varied between 4.5-6%).

In Example 4, an activator (1.5% MgO) was added to the catalyst.

Testing of catalysts

The catalysts were tested in a microreactor by leading purified propylene through a catalyst bed containing 0.2-0.5 g of catalyst. The propylene had been purified by removing the moisture by means of molecular sieves and oxygen by means of BASF's copper catalyst. Chrompack's capillary column (PLOT Fused Silica, liquid phase $\text{Al}_2\text{O}_3/\text{KCl}$, 50 x 0.32 mm) was used in the gas chromatography. During the runs, the propylene flow and the temperature of the reactor tube was often changed for clarifying the effects of these factors. The inlet and outlet gas flow is the same on the small flows used, whereby no pressure occurs in the reactor pipe.

The reactor itself is a quartz glass tube reactor, in which the quantity of the catalyst filling is 1-2 ml. The catalyst is heated in an oven, in which the reactor tube is placed inside a steel tube. The ends of the steel tube are joined with aluminium ears to the poles of the current source, i.e. the tube acts per se as a resistance. The oven is controlled by Eurotherm's controller.

After the oven, the device is connected with an on-line principle to HP's gas chromatograph and an integrator.

Samples are taken with a logic controlled repeater motor from the gas flow and the extra gas flow is led to air conditioning.

Air and nitrogen are used for regenerating and flushing the catalyst.

Tables 1A-1C list the test results when using catalysts according to Example 1 on three different metal contents. Table 2 lists the test results when using catalysts according to Example 2. Tables 3 and 4 list the test results when using reference catalysts according to Examples 3 and 4.

In the Tables, the activity is always shown in the units g of converged propylene/g of metal x h. The percentages of the product distributions are percentages by weight.

TABLE I A

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/g h)
1	6.957	40.284	22.749	30.01	59.72	56.67
4	3.747	51.503	13.977	30.773	48.50	46.03
6	4.923	49.303	16.698	29.076	49.60	48.11
9	5.206	50.399	17.296	27.099	49.60	47.07
12	4.645	53.287	16.411	25.117	46.17	43.82
14	5.75	51.780	17.817	24.828	48.22	45.76
18	5.125	53.575	17.349	23.951	46.43	44.06
23	5.125	54.048	17.349	23.478	45.95	43.61
25	5.087	54.683	16.924	23.306	45.32	43.01

Catalyst $W(O)(t-BuCH_2)_mCl_n$ / silica-alumina (Grace) $m = 1-4$, $n = 4-m$
 Metal content 3.6%

TABLE I D

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/g h)
1	3.389	74.745	11.712	11.025	25.26	46.27
4	5.579	74.653	18.843	1.776	25.35	46.44
7	5.675	74.067	19.479	1.447	25.93	47.51
9	6.201	72.407	20.660	1.397	25.59	50.55
12	6.522	70.917	21.961	1.248	29.08	53.28
14	6.151	72.619	20.585	1.189	27.38	50.16
18	6.623	70.390	22.376	1.232	19.61	54.25
23	6.856	69.605	22.916	1.218	30.40	55.69
27	6.753	66.971	22.655	1.148	30.03	55.02

Metal content 3.6%

Catalyst $W(O)(t-BuCH_2)_2Cl_n / \text{silica} + 1.5\% \text{ of } MgO$ ($n = 1-4$, $n = 4-m$)

TABLE I C

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/g h)
1	14.657	51.898	32.478	0.967	48.10	11.25
4	13.591	50.878	34.591	0.940	49.12	11.49
7	12.576	52.221	34.263	0.040	47.78	11.17
9	12.424	62.687	33.957	0.932	47.31	11.06
12	12.279	54.477	32.296	0.048	42.52	10.64
14	12.115	54.873	32.058	0.965	56.13	10.55
22	11.070	56.064	31.025	0.041	43.94	10.27
27	11.608	57.116	30.331	0.945	42.88	10.03

Metal content 13.5%

Catalyst $W(O)(t-BuCH_2O)_nCl_n$ / silica, (m = 1-4, n = 4-m)

TABLE 2

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/gh)
1	10.678	53.261	34.568	1.493	46.74	26.95
4	10.636	53.622	34.469	1.273	46.38	26.74
7	10.758	53.262	34.272	1.707	46.74	26.15
9	10.654	64.842	13.979	1.536	46.16	26.62
12	10.154	56.023	32.530	1.293	43.98	25.36
18	9.138	60.309	29.324	1.229	39.69	22.81
23.3	9.170	59.990	29.597	1.243	40.01	23.07
28.3	8.046	64.877	26.216	0.861	35.12	20.25

Metal content 6.5%
Catalyst $W(O)(t-BuCH_2)_2Pr_2$ / silica

TABLE 3
(Comparison)

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/g/h)
0.5	7.390	67.688	24.033	0.949	32.31	14.76
4	10.759	59.471	28.846	0.924	40.53	18.52
7	11.015	58.608	29.466	0.511	41.39	18.91
9.5	10.046	58.570	29.580	0.904	41.43	18.53
12	11.082	58.474	29.541	0.503	41.53	18.97
14	10.756	59.178	29.166	0.900	40.82	18.65
20	9.649	62.747	26.740	0.864	37.25	25.11

Metal content 4.9%
Catalyst WO₃ / silica

TABLE 4

Time (h)	Ethene (%)	Propylene (%)	Butenes (%)	Other (%)	Conversion (%)	Activity (g/gh)
1	5.182	80.536	11.362	0.920	19.46	7.69
4	9.030	66.476	23.209	1.286	33.52	13.25
7	10.034	62.474	25.985	1.507	37.53	14.83
9	10.376	65.459	26.643	1.522	38.54	15.23
12	10.417	50.571	27.400	1.512	39.33	15.54
15	10.501	60.126	27.868	1.505	35.87	15.76
20	12.330	54.163	30.134	3.373	45.84	18.11
24	12.755	53.369	30.259	3.617	46.63	18.43
25	12.762	53.410	30.365	3.463	46.59	18.41

Metal content 5.9%
Catalyst WO₃/ silica + 1.5% of MgO

Claims

- 5 1. A catalyst system for metathesis reactions of olefines, which catalyst system comprises a metal carbene complex on a solid carrier, in which the metal carbene complex has the formula:
- $$M(O)_y(RCH_2O)_mX_n$$
- wherein M is W or Mo; R is t-butyl; y is 0 or 1; and
 when y is 0, m = 3 or 4, X is Br and n is from 5 to m; and
 10 when y is 1, m is from 1 to 4, X = Cl and n is from 4 to m.
2. A catalyst system according to Claim 1, in which the metal carbene complex has the formula:
 $W(RCH_2O)_3Br_2$ or $W(RCH_2O)_4Br$, wherein
 R is t-butyl.
- 15 3. A catalyst system according to Claim 1, in which the metal carbene complex has the formula:
 $W(O)(RCH_2O)_mCl_n$ wherein
 R is t-butyl, m is from 1 to 4 and n is from 4 to m.
- 20 4. A catalyst system according to any one of the preceding claims in which the carrier comprises one or more of silica, alumina and magnesium oxide.
5. A catalyst system according to Claim 4, in which the carrier is silica or a mixture of silica and magnesium oxide.
- 25 6. A catalyst system according to any one of the preceding claims, in which the metal-carbene-complex-containing carrier is calcined by heating in a nitrogen, oxygen or hydrocarbon atmosphere.
7. A catalyst system as claimed in Claim 1 substantially as hereinbefore described with reference to the exam-
 30 ples.
8. A process for the metathesis of an olefine in the presence of a catalyst in which the catalyst is as claimed in any one of the preceding claims.
- 35 9. A process as claimed in Claim 8 in which the olefine is propylene.
10. A process as claimed in Claim 8 substantially as hereinbefore described.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3648

DOCUMENTS CONSIDERED TO BE RELEVANT			Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Category	Citation of document with indication, where appropriate, of relevant passages	TECHNICAL FIELDS SEARCHED (Int. CL.5)		
A	EP-A-0 283 400 (SOCIETE NATIONALE ELF AQUITAINE) ----		C 07 C 6/04 B 01 J 31/12	
A	US-A-4 060 468 (K. F. CASTNER) ----			
A	DE-A-1 022 205 (BAYER) ----			
A	EP-A-0 218 138 (MASSACHUSSETTS INSTITUTE OF TECHNOLOGY) -----			
The present search report has been drawn up for all claims				
Place of search THE HAGUE		Date of completion of the search 19-08-1991	Examiner THION M.A.	
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				

EPO FORM 1503 03/81 (P0401)